

What is claimed is:

1. A crosslinked polyrotaxane comprising at least two molecules of polyrotaxane, in which a linear molecule is included in cavities of cyclodextrin molecules in a skewered manner, wherein the linear molecule has at each end a capping group to prevent the dissociation of the cyclodextrin molecules, the at least two molecules of polyrotaxane are crosslinked with each other through physical bonding, and a part or all of hydroxyl groups (-OH) of cyclodextrin molecules are substituted with a non-ionic group(s).
2. A crosslinked polyrotaxane having a reversible ability to respond to external stimulus, which reversibly varies from an uncrosslinked state or crosslinked state to a crosslinked state or uncrosslinked state depending on the presence or absence of an external stimulus, comprising at least two molecules of polyrotaxane, in which a linear molecule is included in cavities of cyclodextrin molecules in a skewered manner, wherein the linear molecule has at each end a capping group to prevent the dissociation of the cyclodextrin molecules, the at least two molecules of polyrotaxane are crosslinked with each other through physical bonding, and a part or all of hydroxyl groups (-OH) of cyclodextrin molecules are substituted with a non-ionic group(s).
3. The crosslinked polyrotaxane according to claim 2, wherein the external stimulus is heat, and the crosslinked polyrotaxane transforms from the uncrosslinked state to a gel state as the crosslinked state in a first temperature range ranging from 5 to 90°C.
4. The crosslinked polyrotaxane according to claim 3, which transforms from the gel state as the crosslinked state to the uncrosslinked state in a second temperature range, which is higher than the first temperature range, and which ranges from 10 to 100°C
5. The crosslinked polyrotaxane according to any one of claims 1 to 4, wherein the non-ionic group is a -OR group, and R is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether

group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

6. The crosslinked polyrotaxane according to any one of claims 1 to 4, wherein the non-ionic group is a -O-R'-X group, and R' is a group resulting from removal of one hydrogen in a linear or branched alkyl group having 1-12 carbons, a group resulting from removal of one hydrogen in a linear or branched alkyl group having 2-12 carbons and at least one ether group, a group resulting from removal of one hydrogen in a cycloalkyl group having 3-12 carbons, a group resulting from removal of one hydrogen in a cycloalkyl ether group having 2-12 carbons or a group resulting from removal of one hydrogen in a cycloalkyl thioether group having 2-12 carbons, and X is OH, NH<sub>2</sub> or SH.

7. The crosslinked polyrotaxane according to any one of claims 1 to 4, wherein the non-ionic group is a -O-CO-NH-R<sub>1</sub> group, and R<sub>1</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

8. The crosslinked polyrotaxane according to any one of claims 1 to 4, wherein the non-ionic group is a -O-CO-R<sub>2</sub> group, and R<sub>2</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

9. The crosslinked polyrotaxane according to any one of claims 1 to 4, wherein the non-ionic group is a -O-Si-R<sub>3</sub> group, and R<sub>3</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

10. The crosslinked polyrotaxane according to any one of claims 1 to 4, wherein

the non-ionic group is a -O-CO-O-R<sub>4</sub> group, and R<sub>4</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

11. The crosslinked polyrotaxane according to any one of claims 1 to 10, wherein substitution of the hydroxyl group with the non-ionic group is 10 to 100% of the total hydroxyl groups of the total cyclodextrin molecules.

12. The crosslinked polyrotaxane according to any one of claims 1 to 11, wherein the cyclodextrin molecule is selected from the group consisting of  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin.

13. The crosslinked polyrotaxane according to any one of claims 1 to 12, wherein the linear molecule is selected from the group consisting of polyethylene glycol, polyisoprene, polyisobutylene, polybutadiene, polypropylene glycol, polytetrahydrofuran, polydimethylsiloxane, polyethylene and polypropylene.

14. The crosslinked polyrotaxane according to any one of claims 1 to 13, wherein the capping group is selected from the group consisting of dinitrophenyl groups, cyclodextrins, adamantane groups, trityl groups, fluoresceins, pyrenes, substituted benzenes, polycyclic aromatics which may be substituted, and steroids.

15. The crosslinked polyrotaxane according to any one of claims 1 to 14, wherein the cyclodextrin molecule is  $\alpha$ -cyclodextrin, and the linear molecule is polyethylene glycol.

16. The crosslinked polyrotaxane according to any one of claims 1 to 15, wherein the linear molecule has the cyclodextrin molecules included in a skewered manner at an amount of 0.001 to 0.6 of a maximum inclusion amount, which is defined as an amount at which the cyclodextrin molecule can be included at maximum when the linear molecule has the cyclodextrin molecules included in a skewered manner, and the amount at maximum is normalized to be 1.

17. A method for preparing a crosslinked polyrotaxane comprising the steps of:
- 1) mixing cyclodextrin molecules and a linear molecule, to prepare a pseudopolyrotaxane in which the linear molecule is included in cavities of the cyclodextrin molecules in a skewered manner;
  - 2) capping each end of the pseudopolyrotaxane with a capping group to prevent the dissociation of the CD molecules, to prepare a polyrotaxane;
  - 3) substituting a part of OH groups of the cyclodextrin molecules with a non-ionic group:
    - A) before the step 1) of mixing to prepare the pseudopolyrotaxane;
    - B) after the step 1) of mixing to prepare the pseudopolyrotaxane and before the step 2) of capping to prepare the polyrotaxane; and/or
    - C) after the step 2) of capping to prepare the polyrotaxane;
  - 4) dissolving at least two molecules of the resultant polyrotaxane in a hydrophilic solvent; and
  - 5) applying an external stimulus to the molecules of the polyrotaxane in the hydrophilic solvent to crosslink the at least two molecules of the polyrotaxane through physical bonding.
18. The method according to claim 17, wherein the external stimulus is heat, and the molecules of polyrotaxane transforms from an uncrosslinked state to a hydrogel state as a crosslinked state in a first temperature range ranging from 5 to 90°C.
19. The method according to claim 18, wherein the molecules of polyrotaxane transforms from the hydrogel state as the crosslinked state to the uncrosslinked state in a second temperature range, which is higher than the first temperature range, and which ranges from 10 to 100°C
20. The method according to any of claims 17 to 19, wherein the polyrotaxane is dissolved so that a weight ratio of the polyrotaxane to the hydrophilic solvent is 0.1:99.9 to 70:30 in the step of dissolving.

21. The method according to any of claims 17 to 20, wherein the step of substituting is set after the step 2) of capping to prepare the polyrotaxane.
22. An external stimulus-responsive material having a reversible ability to respond to external stimulus, which reversibly varies from an uncrosslinked state or crosslinked state to a crosslinked state or uncrosslinked state depending on the presence or absence of an external stimulus, comprising a crosslinked polyrotaxane and a solvent, wherein the crosslinked polyrotaxane comprises at least two molecules of polyrotaxane, in which a linear molecule is included in cavities of cyclodextrin molecules in a skewered manner, wherein the linear molecule has at each end a capping group to prevent the dissociation of the cyclodextrin molecules, wherein the at least two molecules of polyrotaxane are crosslinked with each other through physical bonding, and a part or all of hydroxyl groups (-OH) of cyclodextrin molecules are substituted with a non-ionic group(s).
23. The material according to claim 22, wherein the external stimulus is heat, the solvent is water, and the material transforms from an uncrosslinked state to a crosslinked state, or crosslinked hydrogel state in a first temperature range ranging from 5 to 90°C.
24. The material according to claim 23, wherein the material transforms from the crosslinked state, or crosslinked hydrogel state to the uncrosslinked state in a second temperature range, which is higher than the first temperature range, and which ranges from 10 to 100°C.
25. The material according to any one of claims 22 to 24, wherein a weight ratio of the crosslinked polyrotaxane to the solvent ranges from 0.1 : 99.9 to 70 : 30.
26. The material according to any one of claims 22 to 25, wherein the non-ionic group is a -OR group, and R is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

27. The material according to any one of claims 22 to 25, wherein the non-ionic group is a -O-R'-X group, and R' is a group resulting from removal of one hydrogen in a linear or branched alkyl group having 1-12 carbons, a group resulting from removal of one hydrogen in a linear or branched alkyl group having 2-12 carbons and at least one ether group, a group resulting from removal of one hydrogen in a cycloalkyl group having 3-12 carbons, a group resulting from removal of one hydrogen in a cycloalkyl ether group having 2-12 carbons or a group resulting from removal of one hydrogen in a cycloalkyl thioether group having 2-12 carbons, and X is OH, NH<sub>2</sub> or SH.

28. The material according to any one of claims 22 to 25, wherein the non-ionic group is a -O-CO-NH-R<sub>1</sub> group, and R<sub>1</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

29. The material according to any one of claims 22 to 25, wherein the non-ionic group is a -O-CO-R<sub>2</sub> group, and R<sub>2</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

30. The material according to any one of claims 22 to 25, wherein the non-ionic group is a -O-Si-R<sub>3</sub> group, and R<sub>3</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12 carbons or a cycloalkyl thioether group having 2-12 carbons.

31. The material according to any one of claims 22 to 25, wherein the non-ionic group is a -O-CO-O-R<sub>4</sub> group, and R<sub>4</sub> is a linear or branched alkyl group having 1-12 carbons, a linear or branched alkyl group having 2-12 carbons and at least one ether group, a cycloalkyl group having 3-12 carbons, a cycloalkyl ether group having 2-12

carbons or a cycloalkyl thioether group having 2-12 carbons.

32. The material according to any one of claims 22 to 31, wherein substitution of the hydroxyl group with the non-ionic group is 10 to 100% of the total hydroxyl groups of the total cyclodextrin molecules.

33. The material according to any one of claims 22 to 32, wherein the cyclodextrin molecule is selected from the group consisting of  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin.

34. The material according to any one of claims 22 to 33, wherein the linear molecule is selected from the group consisting of polyethylene glycol, polyisoprene, polyisobutylene, polybutadiene, polypropylene glycol, polytetrahydrofuran, polydimethylsiloxane, polyethylene and polypropylene.

35. The material according to any one of claims 22 to 35, wherein the capping group is selected from the group consisting of dinitrophenyl groups, cyclodextrins, adamantane groups, trityl groups, fluoresceins, pyrenes, substituted benzenes, polycyclic aromatics which may be substituted, and steroids.

36. The material according to any one of claims 22 to 35, wherein the cyclodextrin molecule is  $\alpha$ -cyclodextrin, and the linear molecule is polyethylene glycol.

37. The material according to any one of claims 22 to 36, wherein the linear molecule has the cyclodextrin molecules included in a skewered manner at an amount of 0.001 to 0.6 of a maximum inclusion amount, which is defined as an amount at which the cyclodextrin molecule can be included at maximum when the linear molecule has the cyclodextrin molecules included in a skewered manner, and the amount at maximum is normalized to be 1.